

(19) World Intellectual Property Organization
International Bureau



(43) International Publication Date
8 April 2004 (08.04.2004)

PCT

(10) International Publication Number
WO 2004/030109 A1

(51) International Patent Classification⁷: H01L 33/00,
C09K 11/465, 11/477

State and Materials Chemistry, Eindhoven University of Technology, P.O.Box 513, NL-5600 MB Eindhoven (NL). HINTZEN, Hubertus, T. [NL/NL]; c/o Laboratory of Solid State and Materials Chemistry, Eindhoven University of Technology, P.O.Box 513, NL-5600 MB Eindhoven (NL). LI, Yuan-Qiang [CN/NL]; c/o Laboratory of Solid State and Materials Chemistry, Eindhoven University of Technology, P.O.Box 513, NL-5600 MB Eindhoven (NL).

(21) International Application Number:
PCT/EP2003/010599

(22) International Filing Date:
23 September 2003 (23.09.2003)

(25) Filing Language: English

(74) Agent: POKORNY, Gerd; c/o Osram GmbH, Postfach 22 16 34, 80506 München (DE).

(26) Publication Language: English

(81) Designated States (national): CN, JP, US.

(30) Priority Data:
02021172.8 24 September 2002 (24.09.2002) EP

(84) Designated States (regional): European patent (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IT, LU, MC, NL, PT, RO, SE, SI, SK, TR).

(71) Applicant (for all designated States except US): OSRAM OPTO SEMICONDUCTORS GMBH [DE/DE]; Wernerwerkstr. 1, 93040 Regensburg (DE).

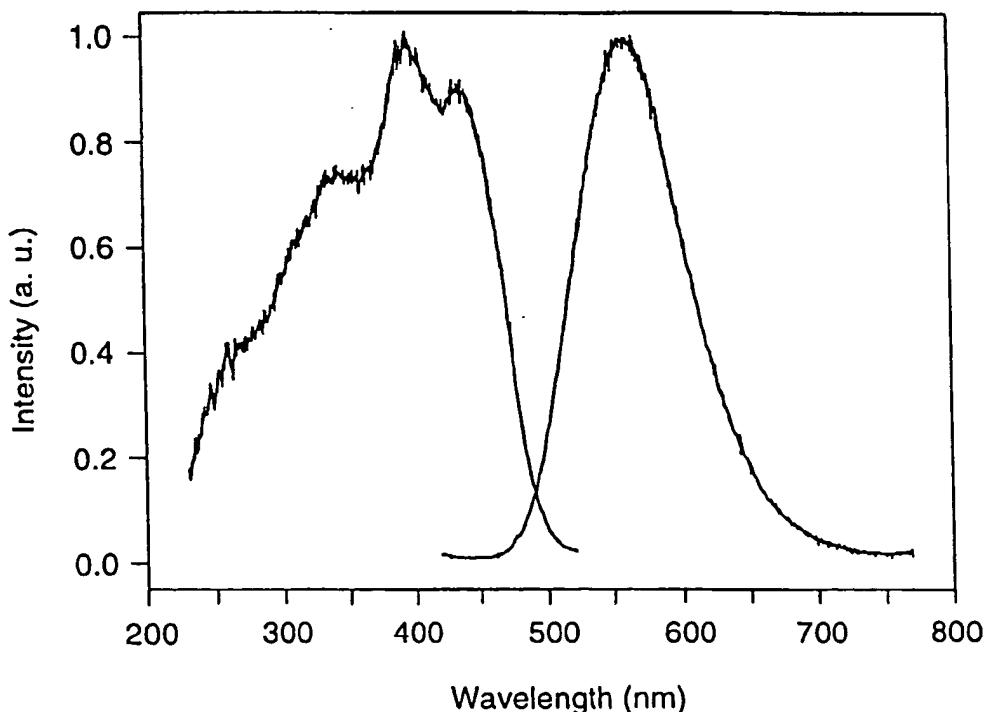
Published:

— with international search report

(72) Inventors; and
(75) Inventors/Applicants (for US only): DELSING, Anne, Charlotte, Antoinette [NL/NL]; c/o Laboratory of Solid

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

(54) Title: LUMINESCENT MATERIAL, ESPECIALLY FOR LED APPLICATION



WO 2004/030109 A1

(57) Abstract: UV-blue excitable green luminescent material consisting of a Eu-doped oxynitride host lattice with general composition $MSi_2O_2N_2$, wherein M is at least one of an alkaline earth metal chosen from the group Ca, Sr, Ba.

Title:Luminescent material, especially for LED application**Technical Field**

This invention relates to a luminescent material which is excitable in the UV-blue part of the spectral region, and more particularly, but not exclusively to
5 a phosphor for light sources, especially for Light Emitting Diodes (LED). The phosphor belongs to the class of rare-earth activated silicon oxynitrides.

Background Art

So far white LEDs were realized by combining a blue-emitting diode with a yellow emitting phosphor. Such a combination has a poor color rendition, which, however, can be improved significantly by using a red-green-blue
10 system (RGB). Such a system uses for example a red and blue emitter in combination with a green-emitting aluminate phosphor, like $\text{SrAl}_2\text{O}_4:\text{Eu}$ or $\text{BaAl}_2\text{O}_4:\text{Eu}$, with the possible addition of Mn to Eu, whose emission maximum is around 520 nm, see US-A 6 278 135. However, the position of the excitation and emission bands of these aluminates is not optimum. They have
15 to be excited by short UV in the range of 330 to 400 nm.

On the other hand, some phosphors derived from the class of MSiON are known; see e.g. „On new rare-earth doped M-Si-Al-O-N materials“ by van Krevel, TU Eindhoven 2000, ISBN 90-386-2711-4, Chapter 6. They are doped with Tb. Emission is achieved upon excitation by 365 nm or 254 nm.

Disclosure of the Invention

It is an object of the present invention to provide a new luminescent material. A further object is to provide a phosphor with a fine-tuned green emission which can be efficiently excited by UV/blue radiation. A further object is to provide a phosphor for use in an illumination device with at least one LED as

5 light source, the LED emitting primary radiation in the range from 380 to 470 nm, this radiation being partially or completely converted into longer-wavelength radiation by such phosphors which are exposed to the primary radiation of the LED. A further object is to provide an illumination device which emits white light and in particular has a high color rendering. A further object is to provide a high-efficiency illumination device like a LED device which absorbs well in the range from 380 to 470 nm and is easy to produce.

10

15

These objects are achieved by the characterizing features of claim 1 and 8, respectively. Particularly advantageous configurations are given in the dependent claims.

The conversion is achieved at least with the aid of a phosphor which originates from the class of the Eu- or Eu,Mn-coactivated silicone oxynitrides. In more detail, a novel phosphor material is created by doping $MSi_2O_2N_2$ (M = Ca, Sr, Ba) host lattices with Eu ions. The obtained phosphors show high

20 chemical and thermal stability.

More extended fine tuning of all relevant properties can be obtained by partial replacement up to 40%, the certain percent proportion given as x, of group (SiN) by (AlO), resulting in a general composition given by $MSi_{2-x}Al_xO_{2+x}N_{2-x}$. the preferred range is 1 to 15% (x = 0,01 to 0,15).

25 Preferably, the metal M is Ca or at least mainly Ca with minor additions of Ba and/or Sr for a green-emitting material which can be efficiently excited

with blue radiation. The incorporation of nitrogen increases the degree of covalent bonding and ligand-field splitting. As a consequence this leads to a shift of excitation and emission bands to longer wavelengths compared to oxide lattices. The obtained phosphors show high chemical and thermal stability.

More extended fine tuning of all relevant properties can be obtained by use of a cation M which is achieved by combining several of said M metals, by inclusion of Zn as part of cation M, preferably up to 5 - 40 mol-% of M, and/or at least partial replacement of Si by Ge. The amount of Eu doped to cation M is a partial replacement of between 0,1 and 25 %, preferably between 2 and 15% of M. In addition, under the assumption of a given amount of Eu, further doping with Mn for fine-tuning of relevant properties is possible with an preferred amount of at most 50% of the given Eu doping.

Since these materials can convert UV-blue radiation into green light due to low-energy excitation bands, they can be applied for example in white light sources (e.g. lamps), especially based on primarily blue-emitting LEDs (typically based on GaN or InGaN with emission around 430 to 470 nm) combined with a red-emitting phosphor. A suitable red-emitting phosphor is a Eu-doped silicon nitride material, like $M_2Si_5N_8$ (M = Ca, Sr, Ba), see for example WO 01/40403. Also application for colored light sources is possible.

Brief Description of the Drawings

In the text which follows, the invention is explained in more detail with reference to a plurality of exemplary embodiments. In the drawings:

Figure 1 shows a semiconductor component (LED) which serves as light source for white light, with casting resin (Figure 1a) and without casting resin (Figure 1b);

Figure 2 shows an illumination device with phosphors in accordance with the present invention;

Figure 3 to 5 show the emission spectra and reflection spectra of phosphors in accordance with the present invention.

Best Mode for Carrying Out the Invention

- 5 By way of example, a structure similar to that used in WO 01/40403 is described for use in a white LED together with an InGaN chip. The structure of such a light source for white light is specifically shown in Figure 1a. The light source is based on a semiconductor component (chip 1) of type InGaN with a peak emission wavelength of 400 nm, having a first and a second electrical connection 2,3, which is embedded in an opaque base housing 8 in the region of a recess 9. One of the connections 3 is connected to the chip 1 via a bonding wire 4. The recess has a wall 7 which serves as reflector for the blue primary radiation of the chip 1. The recess 9 is filled with a potting compound 5 which contains a silicone casting resin (or epoxy casting resin) as its main constituents (pref. at least 80 % by weight) and further comprises phosphor pigments 6 (pref. less than 15% by weight). There are also further small amounts of, inter alia, methyl ether and Aerosil. The phosphor pigments are a mixture of three pigments which emit blue, green and red light with the green phosphor being in accordance with the invention.
- 10
- 15
- 20
- 25

Fig. 1b shows an embodiment of a light source with a semiconductor component 10 in which the conversion into white light is effected by means of phosphor conversion layers 16 which are applied directly to the individual chip. On top of a substrate 11 there are a contact layer 12, a mirror 13, a LED chip 14, a filter 15 and a phosphor layer 16, which is excited by the primary radiation of the LED, and converts it into visible long-wave radiation. This structural unit is surrounded by a plastic lens 17. Only the upper contact 18

of the two ohmic contacts is illustrated. Primary UV radiation of the LED is around 400 nm and secondary radiation is emitted by a first phosphor in accordance with the invention using $\text{BaSi}_2\text{O}_2\text{N}_2\text{:Eu}$ emitting around 500 nm and by a second phosphor using a Nitridosilicate emitting orange-red.

5 Figure 2 shows an illumination device 20. It comprises a common support 21, to which a cubical outer housing 22 is adhesively bonded. Its upper side is provided with a common cover 23. The cubical housing has cutouts in which individual semiconductor components 24 are accommodated. They are blue emitting light-emitting diodes with a peak emission of around 450 to 470 nm.

10 The conversion into white light takes place by means of conversion layers 25 which are arranged on all the surfaces which are accessible to the blue radiation. These include the inner surfaces of the side walls of the housing, of the cover and of the support. The conversion layers 25 consist of phosphors which emit in the red spectral region, and in the green spectral region using a phosphor according to the invention and mixing up together with the non-absorbed part of the primary radiation blue primary into white light.

15

Eu₂O₃ (with purity 99.99%), BaCO₃ (with purity > 99.0%), SrCO₃ (with purity > 99.0%), CaCO₃ (with purity > 99.0%), SiO₂ and Si₃N₄ were used as commercially available starting materials for the production of the new inventive phosphors. The raw materials were homogeneously wet-mixed in the appropriate amounts by a planetary ball mill for 4-5 hours in isopropanol. After mixing the mixture was dried in a stove and ground in an agate mortar. Subsequently, the powders were fired in molybdenum crucibles at 1100-1400 °C under a reducing nitrogen/hydrogen atmosphere in a horizontal tube furnace. After firing, the materials were characterized by powder X-ray diffraction (copper K-alpha line).

All samples show efficient luminescence under UV-blue excitation with emission maxima in the blue-green (in case of M = Ba), green (M = Ca) or

yellow-green (M = Sr). Typical examples of emission and excitation spectra can be seen in Fig. 3 (M = Ca), Fig. 4 (M = Sr) and Fig. 5 (M = Ba). For CaSi₂O₂N₂:Eu a green-emitting phosphor (560 nm peakemission) is obtained, which can be efficiently excited in the blue part of the spectrum (excitation 5 maximum at about 440 nm). By using a mixed compound with M = (Ba,Sr) and varying the proportion of Ba and Sr, the emission can be shifted in the range 500-570 nm, while the top of the excitation band can be shifted from 400 nm up to 430 nm. The observed shift to higher wavelengths is ascribed to a center of gravity of the Eu 5d band at lower energy and a stronger ligand- 10 field splitting of the Eu 5d band. Additional manipulation can be achieved by at least partial replacement (for example up to 15 mol-%) of (SiN) by (AlO), resulting in a preferred structure MSi_{2-x}O_{2+x}Al_xN_{2-x}:Eu (e.g. x = 0,15).

Since these materials can convert UV-blue radiation into green light due to low-energy excitation bands, they can be applied in white light sources, for 15 example based on primarily blue-emitting LEDs (typically GaN or InGaN) combined with a red-emitting phosphor.

Additional fine tuning can be achieved by incorporation of Zn as an addition to cation M, preferably not more than 30%, and at least partial replacement of Si by Ge, preferably not more than 25 %.

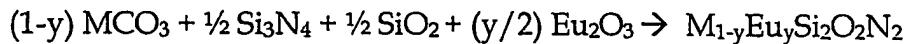
20 Table 1

Raw materials	Grade
MCO ₃ (M = Ca, Sr, Ba)	99.0%
SiO ₂	Aerosil OX50
γ-Al ₂ O ₃	> 99.995

Si ₃ N ₄	β content: 23.3%, O ~ 0.7%
Eu ₂ O ₃	99.99%

In the following the synthesis procedures are given. Possible starting materials are shown in table 1.

All the oxynitride phosphors can be synthesized according to the following
5 reaction equation:



with (M = Ca, Sr, Ba). For example y = 0,1.

The powder mixture is fired for several hours in Mo crucibles at 1100-1400 °C
in a reducing atmosphere of mainly N₂ with small amounts of H₂ (10%) in
10 horizontal tube furnaces.

With the atomic radius decreasing from Ba to Ca it was found that the replacement of (SiN)⁺ by (AlO)⁺ by this reaction became easier.

Figure 3 shows a typical emission/excitation spectra of CaSi₂O₂N₂:Eu.

Figure 4 shows a typical emission/excitation spectra of SrSi₂O₂N₂:Eu.

15 Figure 5 shows a typical emission/excitation spectra of BaSi₂O₂N₂:Eu.

Doping with Eu was 10% of cation M in all embodiments.

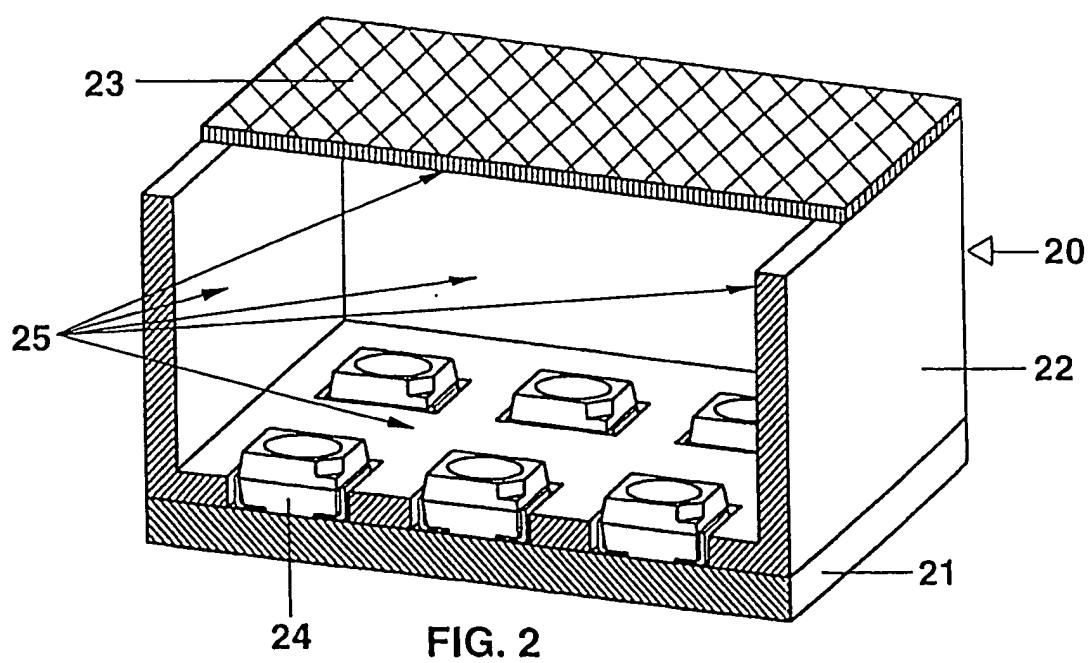
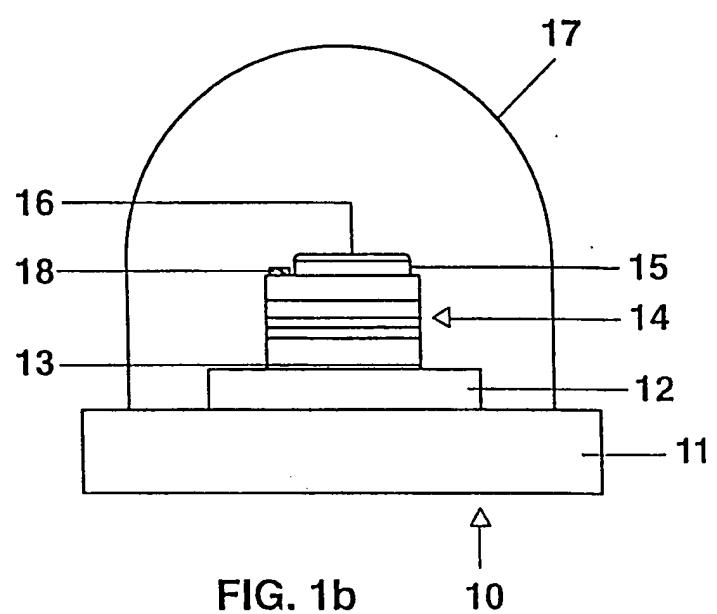
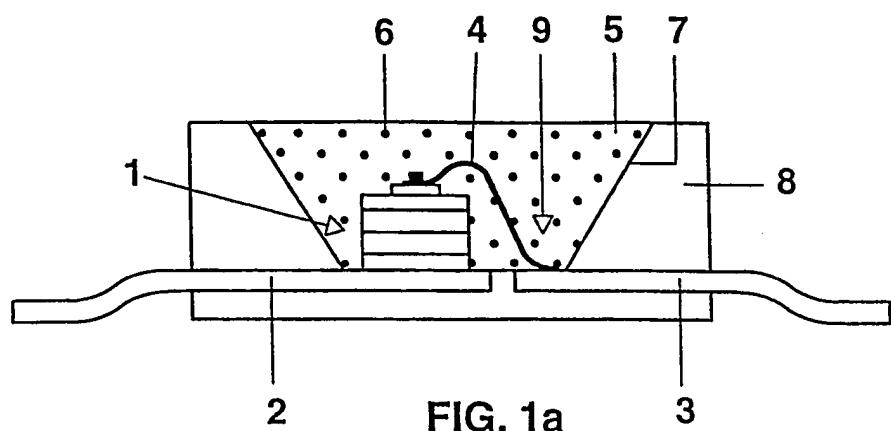
The peak emission for M = Ca was around 560 nm, and for M = Sr it was around 570 nm, and for M = Ba it was around 500 nm.

Claims**What is claimed is:**

1. Luminescent material, especially a phosphor for LED-applications, which is excitable in the UV-blue region from 380 to 470 nm, characterized by a Eu-doped host lattice with general composition $MSi_2O_2N_2$, wherein M is at least one of an alkaline earth metal chosen from the group Ca, Sr, Ba and with a proportion of Eu from 0,1 to 30% of M.
5
2. UV-blue excitable luminescent material according to claim 1, wherein M is Calcium in order to achieve green emission.
3. UV-blue excitable luminescent material according to claim 1, wherein M is a mixture of at least two of these metals.
- 10 4. UV-blue excitable luminescent material according to claim 1, wherein M comprises in addition Zn, preferably up to 40 mol-%.
5. UV-blue excitable luminescent material according to claim 1, wherein Si is replaced fully or partially by Ge, preferably up to 25 mol-%.
- 15 6. UV-blue excitable luminescent material according to claim 1, wherein the host material is further doped with Mn, the amount of Mn being preferably at most up to 50% of the Eu doping.
7. UV-blue excitable luminescent material according to claim 1, wherein SiN is partially replaced by AlO, resulting in a general composition given by $MSi_{2-x}Al_xO_{2+x}N_{2-x}$.
- 20 8. Light source (20) with a UV-blue excitable luminescent material according to one of the preceding claims.

- 9 -

9. Light source according to claim 8, wherein the primary emitted light is blue and the UV-blue excitable luminescent material according to claims 1-7 is combined with other phosphors, esp. a red emitting phosphor, in order to convert part of the primary emitted light into secondary emitted light of longer wavelength resulting in emitting white light.
5
10. Light source according to claim 8, wherein the primary emitted radiation is UV and the UV-blue excitable luminescent materials according to claims 1-7 are combined with other phosphors, esp. a red and a blue emitting phosphor, in order to convert the primary emitted radiation into secondary emitted light of longer wavelength resulting in emitting white light.
10
11. Light source according to claim 8, wherein the light source is an illuminating device with at least one LED.



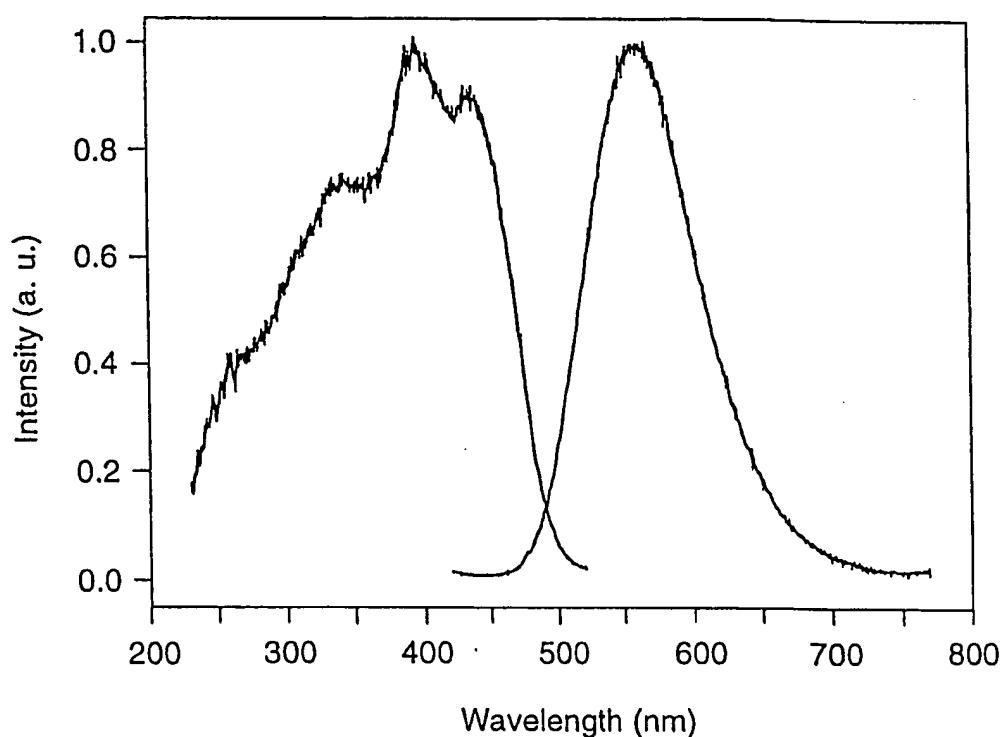


FIG. 3

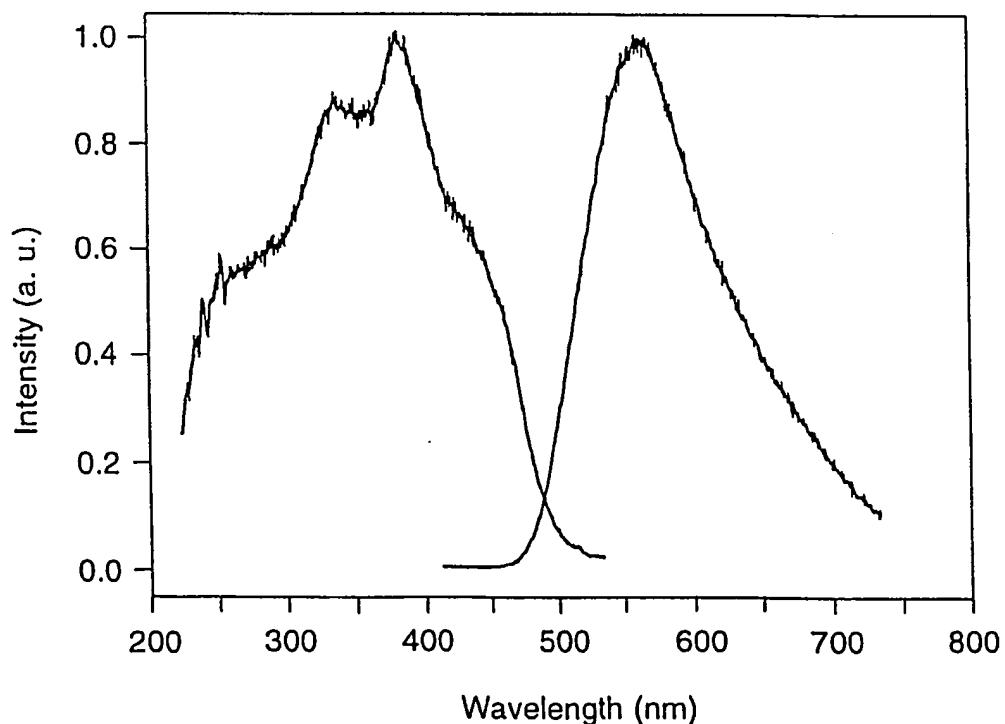


FIG. 4

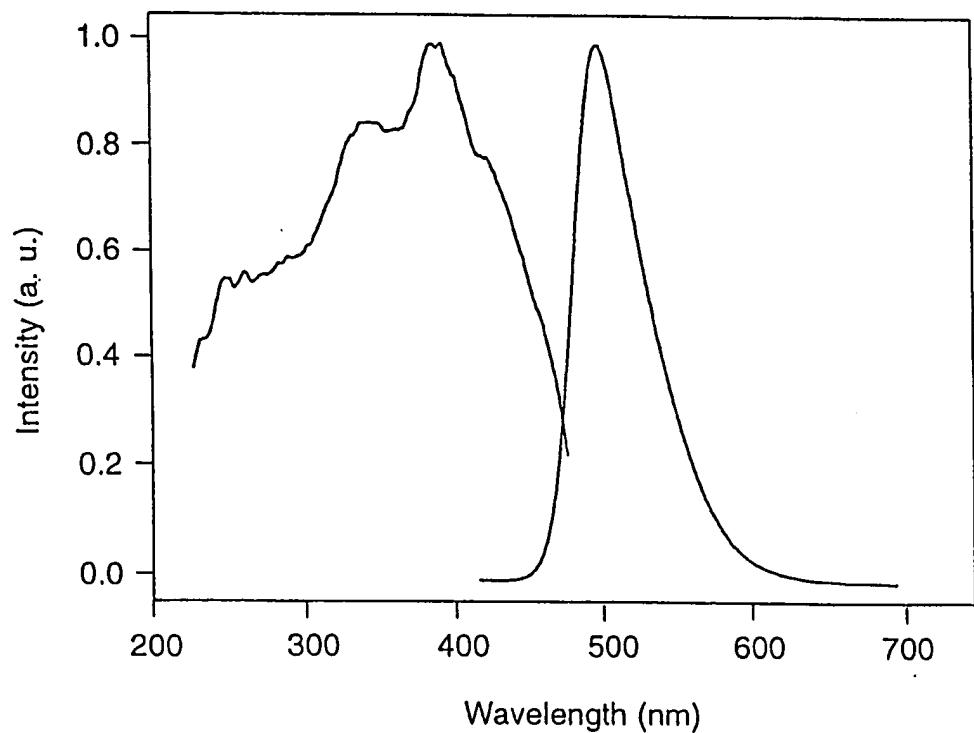


FIG. 5

INTERNATIONAL SEARCH REPORT

PCT/EP 03/10599

A. CLASSIFICATION OF SUBJECT MATTER
 IPC 7 H01L33/00 C09K11/465 C09K11/477

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
 IPC 7 C09K

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 6 255 670 B1 (DUGGAL A ET AL) 3 July 2001 (2001-07-03) the whole document ----	1-4,6, 8-11
A	EP 1 193 306 A (SUMITOMO CHEMICAL CO) 3 April 2002 (2002-04-03) claim 1 ----	1,3-6
A	EP 1 104 799 A (PATRA PATENT TREUHAND) 6 June 2001 (2001-06-06) claims 1,6 ----	1,4,5
A	US 2002/043926 A1 (KAGA K ET AL) 18 April 2002 (2002-04-18) the whole document ----	1,7-11

Further documents are listed in the continuation of box C.

Patent family members are listed in annex.

* Special categories of cited documents :

- *A* document defining the general state of the art which is not considered to be of particular relevance
- *E* earlier document but published on or after the international filing date
- *L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- *O* document referring to an oral disclosure, use, exhibition or other means
- *P* document published prior to the international filing date but later than the priority date claimed

- *T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- *X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- *Y* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- *&* document member of the same patent family

Date of the actual completion of the international search

6 January 2004

Date of mailing of the international search report

13/01/2004

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
 NL - 2280 HV Rijswijk
 Tel: (+31-70) 340-2040, Tx. 31 651 epo nl,
 Fax: (+31-70) 340-3016

Authorized officer

van der Linden, J.E.

INTERNATIONAL SEARCH REPORT

PCT/EP 03/10599

Patent document cited in search report		Publication date		Patent family member(s)		Publication date
US 6255670	B1	03-07-2001	US	6294800 B1		25-09-2001
EP 1193306	A	03-04-2002	CN EP JP US	1345908 A 1193306 A2 2002332481 A 2002038861 A1		24-04-2002 03-04-2002 22-11-2002 04-04-2002
EP 1104799	A	06-06-2001	EP CA CA CN CN WO WO EP EP HU HU JP JP TW US US	1104799 A1 2359896 A1 2360330 A1 1337988 T 1337989 T 0140403 A1 0139574 A1 1238041 A1 1153101 A1 0105080 A2 0200436 A2 2003515655 T 2003515665 T 524840 B 2003024438 A1 2003020101 A1		06-06-2001 07-06-2001 07-06-2001 27-02-2002 27-02-2002 07-06-2001 07-06-2001 11-09-2002 14-11-2001 29-04-2002 29-06-2002 07-05-2003 07-05-2003 21-03-2003 06-02-2003 30-01-2003
US 2002043926	A1	18-04-2002	JP	2002076434 A		15-03-2002